

UCD CSN Technical Instruction #402B

Carbon Analysis Daily Operation

*Chemical Speciation Network
Air Quality Research Center
University of California, Davis*

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DOCUMENT HISTORY

Date Modified	Initials	Section/s Modified	Brief Description of Modifications
4/2/2020	XZ	6.1, 9	Minor update on terminology for consistency. Updated QC chart examples.
5/11/2021	RG, AB, JG	9	Updated procedure used for daily blanks and sucrose standard checks, running sample and sample replicates, and weekly performance check

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1. PURPOSE AND APPLICABILITY

The subject of this technical instruction document (TI) is daily operation of the carbon analyzers for the Chemical Speciation Network (CSN). The scope is to ensure good laboratory practices while performing carbon analysis of quartz filter.

2. SUMMARY OF THE METHOD

Carbon content is measured from quartz fiber filters using thermal/optical transmission-reflectance spectrometry. These instruments, referred to as carbon analyzers, are prepared for each day of analysis. Punches from quartz filters are inserted into the carbon analyzers, where they undergo a specified heating protocol. The thermograms generated during analysis provide the means for carbon content quantification.

3. DEFINITIONS

- **Flame Ionization Detector (FID):** The detector used in the carbon analyzer instruments.
- **Quality Control (QC):** Methods for maintaining acceptable levels of measurement quality.
- **Quartz Blanks (QB):** Quartz filters maintained in the laboratory that have not been exposed to sampling conditions.
- **Total Carbon (TC):** The total estimated carbon content of the sample derived from the measured carbon fractions.

4. HEALTH AND SAFETY WARNINGS

4.1 Laser Safety

The Sunset Laboratory OCEC Carbon Aerosol Analyzers uses a 658 nm laser diode for the optical light source during the sample analysis. While the analyzer itself is classified as a Class 1 Laser Product, meaning that there is no harmful laser radiation exposure to the operator during normal operation and maintenance., the internal source laser diode is rated as a Class 3b product and emits sufficient optical power to constitute a possible hazard to the human eye if directly exposed to the laser beam. Therefore, all repair and service must be performed by a trained technician.

4.2 Gas Cylinders

It is recommended that the lab technicians use caution when handling all support gas cylinders and regulators, and always have cylinders properly chained to a safety rack.

NOTE: Hydrogen is a flammable gas and extra precautions should be used with the hydrogen gas lines from the supply cylinder to ensure all fittings are connected and must be leak tested each time a new cylinder is installed. The pressure of the hydrogen gas line should be kept under 15 psi at all times.

5. CAUTIONS

Not applicable.

6. INTERFERENCES

6.1 Pyrolytically-Produced Elemental Carbon (OP)

Laser transmittance and reflectance signals are used to optically correct for pyrolytically-produced elemental carbon (or char or OP) formed from organic compounds during the initial non-oxidizing stage of the analysis. Formation of OP decreases the transmittance/reflectance of the laser beam through the system. During the second (oxidizing) stage of the analysis, all EC (including OP) is oxidized from the filter. The split point between OC and EC is determined during the oxidation of EC when the transmittance or reflectance of the laser beam rises back to its initial value at the beginning of the analysis. Once the point is found, the EC that evolves after this point is quantitatively equal to the original EC of the sample. OP is defined as carbon evolved between the addition of oxygen and the OC/EC split point. It is assumed that the OP and the original EC have the same light absorption efficiency and that the OP evolves from the filter media earlier than the original EC. If the OC/EC split occurs before the addition of oxygen, OP is zero and peak of OC4 ends at the split time.

6.2 Carbonate Carbon

Carbonate carbon (from calcium carbonate) is volatilized near the end of the first (or non-oxidizing) heating stage and is therefore initially included in the OC quantification. The FID response for the distinctive carbonate peak can be integrated manually and subtracted from the total area assigned to OC, which allows calculation of separate values for organic and carbonate carbon. Alternatively, a separate filter punch can be exposed to hydrogen chloride (HCl) vapors (which react with carbonate to form gaseous CO₂ and removes carbonate carbon from the filter) and organic and elemental carbon can be quantified (in the absence of carbonate carbon) in a second analysis. The first method is usually adequate for PM_{2.5} samples and can be accomplished with a single analysis.

NOTE: Carbonate carbon is not generally present in PM_{2.5} at quantities above the absolute uncertainty of the method.

7. PERSONNEL QUALIFICATIONS

Only trained lab personnel designated by the Laboratory Manager may operate the carbon analyzers or perform sample preparation in the carbon laboratory.

8. EQUIPMENT AND SUPPLIES

- Thermal-Optical Transmittance/Reflectance Carbon Aerosol Analyzer (Sunset Laboratory Inc.)
- Quartz filters
- Precision Punch
- Automatic pipettes, 10-100 μ L, 100-1000 μ L
- Forceps, stainless steel tipped, silicone tipped
- Pre-fired quartz fiber filters
- Volumetric flasks, 10mL, 100mL
- Analytical balance

- Porcelain evaporating dish
- Helium, ultra-high purity
- Hydrogen, ultra-high purity
- Oxygen (10 %) in helium, premixed, purified
- Methane (5 %) in helium, premixed, purified
- Air, Ultra Zero
- Sucrose, 99.5 % reagent grade
- Organic-free water, generated in-house with a deionized water unit (DI water, MilliQ Academic)

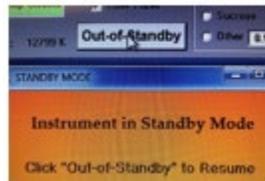
9. PROCEDURAL STEPS

Start instrument from standby mode.

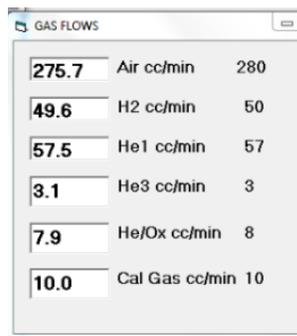
1. Check the gas cylinder pressures and record the values on the “Gas Pressure Table”. The pressures should be very similar to the last records from the end of the day before. If there is a leak, do not proceed and notify lab manager.

NOTE: Cylinder change is required if the pressure is below 100 psi. Refer to the instructions for changing gas cylinders.

2. If the instrument is in “Standby” mode, click on the **Out-of-Standby** button in the top window.



3. Wait 10-15 seconds for the gas flows to stabilize. The actual gas flows should be close to their pre-set values.

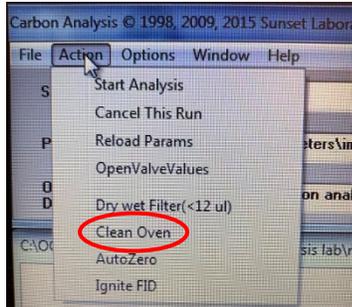


Actual Value	Gas Type	Setpoint Value
275.7	Air cc/min	280
49.6	H2 cc/min	50
57.5	He1 cc/min	57
3.1	He3 cc/min	3
7.9	He/Ox cc/min	8
10.0	Cal Gas cc/min	10

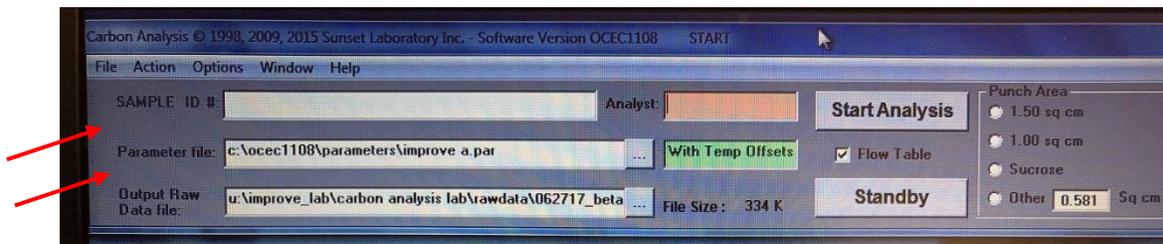


4. Push the red ignition button on the methanator to light the FID. A soft “pop” sound usually occurs with the FID lighting. Wait for the FID signal reading to increase above zero. If not, repeat the ignition.

5. Click the “Click Here when FID flame lights” button on the software screen once the FID is lit.
6. Click on “Action” menu and select “Clean Oven”. The chamber should be closed at this time.



7. Verify the parameter file “improve a.par” (or the latest version of improve a.par with a timestamp) is selected in the “Parameter file” box.



8. Verify the output raw data file is stored under directory U:\CSN\Carbon analyzers\InstantData. Start a new output file daily with the following name format: MMDDYYYY_ANALYZER NAME.txt
9. Take the QC|QB (quartz blank filter) container, sucrose solution #15 (concentration closest to CSN median values), and the sample trays for the day’s analysis out of refrigerator. The sucrose solution and samples should be kept at room temperature for at least 30 min before analysis.

Running blanks:

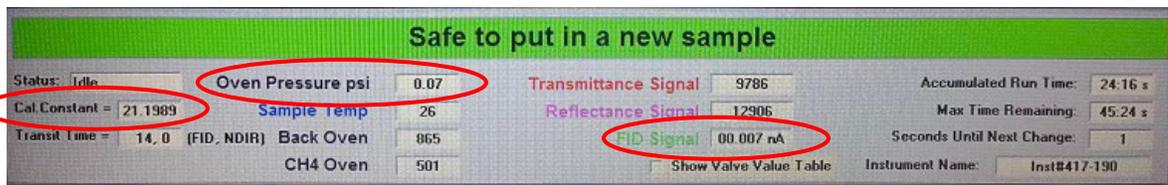
1. Clean the benchtop working area with laboratory wipes. Prepare the sample punch area by covering the clear plastic dish with cutting board on the benchtop with a piece of unused aluminum foil. Use foil to cover the tray under the ball joint for each instrument.

- While the computer is in “Safe to put new sample” mode, remove the front oven clamp and ball joint cap and gently remove the quartz sample holder from the oven with the metal forceps. Let the sample holder rest on the support.
- Take a pre-fired quartz filter from the QC|QB container and carefully clean the edge of the precision punch.
- Take another pre-fired quartz filter from the QC|QB container and place it in the sample punch area. Use the precision punch to remove a section from the blank quartz filter and load the filter punch onto the sample holder and into the main oven via the ball joint. Make sure the proper side (rough side) is facing up while placed centrally into the sample holder’s designated area.

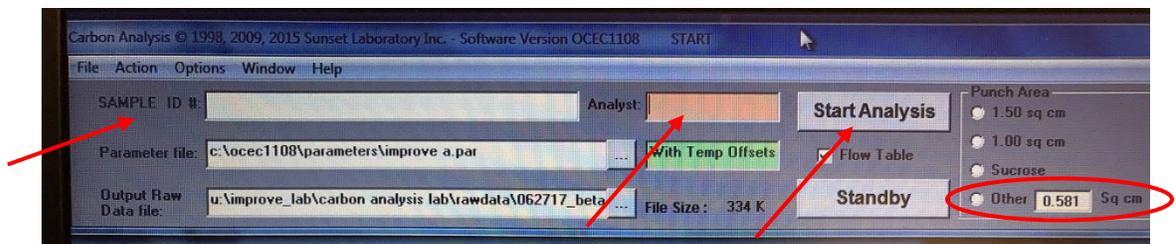


NOTE: The operator should be able to make four punches on a 25 mm blank filter. The fifth and sixth punches can be made with a new blank filter. Put this filter back to the container after taking out the punch for future use.

- In the software, verify that the correct Cal. Constant value is typed in, the initial oven pressure meets the minimum threshold value and FID signal reading is above 0.



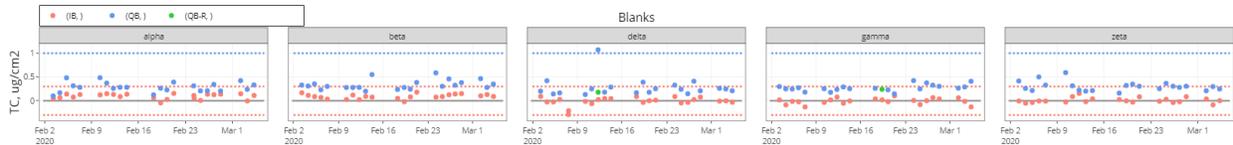
- Type in “QC|QB” in the Sample ID# box and type in the operator’s initial in the Analyst box. Select “Other 0.568 sq cm” (or the most updated punch area) as the punch area and click **Start analysis**.



- After finishing analysis of QC|QB, check Total Carbon (TC) concentration of “QC|QB” on the QC touchscreen. If $TC \leq 1.0 \mu\text{gC}/\text{cm}^2$, proceed with running an instrument blank (QC|IB) without taking the filter punch out of the oven. Type in “QC|IB” in the Sample ID# box and select **Other 0.568 sq cm** (or the most updated punch area) as the punch area and click **Start analysis**. Otherwise, repeat the filter blank analysis with Sample ID

being “QC|QB-R”. If the second analysis fails to meet the criteria, make a note in the paper logbook and proceed with QC|IB analysis.

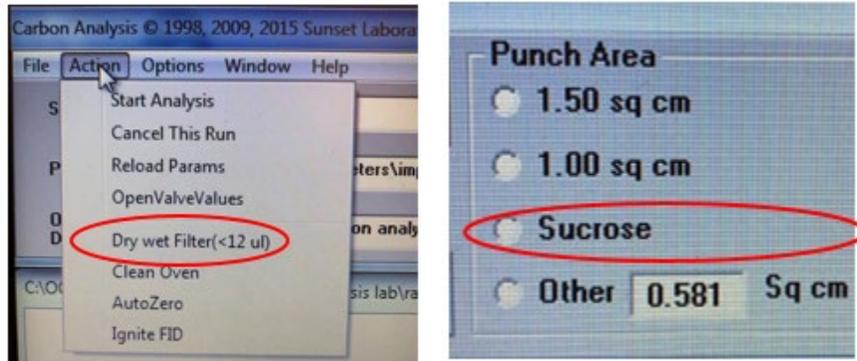
8. After finishing analysis of QC|IB, check Total Carbon (TC) concentration of “QC|IB” on the QC touchscreen. If $-0.3 \leq TC \leq 0.3 \text{ } \mu\text{gC}/\text{cm}^2$, proceed with running a sucrose standard. Otherwise, repeat the instrument blank analysis with Sample ID being the same. If the second analysis fails to meet the criteria, pause analysis on this instrument and notify lab manager.



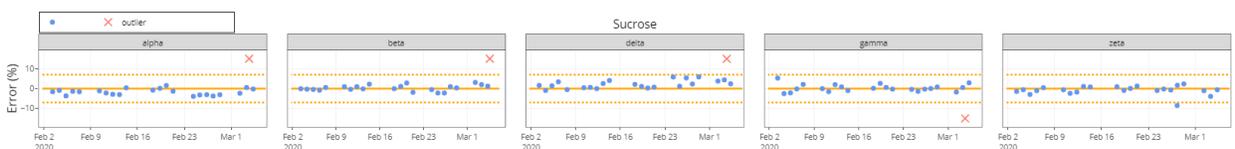
Running daily sucrose standard:

1. For daily sucrose standard checks, use the pre-made sucrose solution #15 stored in the refrigerator. Sucrose standard solutions are made by dissolving a certain amount of sucrose solids in MilliQ water and diluting to desired concentrations. Related instructions and the calculation template can be found in the UCD_Carbon 402H TI- Sucrose Generation.
2. Remove the front oven clamp and ball joint cap and gently remove the quartz sample holder from the main oven with the metal forceps. Let the sample holder rest on the support.
3. Use the calibrated pipettor to dispense 10.0 μL of the sucrose solution to the center of the filter punch without removing the punch from the sample holder. When pipetting, ensure all liquid comes out of the tip by pressing the button down to a full stop. Gently touch the tip of the pipette to the filter to dispense any remaining liquid.
4. Gently slide the sample holder back into the oven and seal the ball joint with the O-ring, oven cap, and clamp.
5. Click on “**Action**” menu and select “**Dry wet filter (<12 μL)**”.





6. Scan the barcode of “QC|Sucrose|15” in the Sample ID# box and select **Sucrose** as the punch area and start analysis.
7. After the instrument finishes with sucrose analysis, check QC touchscreen for measurement error. If the error is within $\pm 7\%$, proceed with running samples. Otherwise, repeat the sucrose standard analysis with the Sample ID name being “QC|Sucrose-R|15”. If the second analysis fails to meet the criteria, pause analysis on this instrument and notify the lab manager.



Running a sample:

1. While the computer is in “Safe to put in a new sample” mode, remove the front oven clamp and ball joint cap and gently remove the quartz sample holder from the oven with the metal forceps. Let the sample holder rest on the support. Remove the filter punch from the last run.

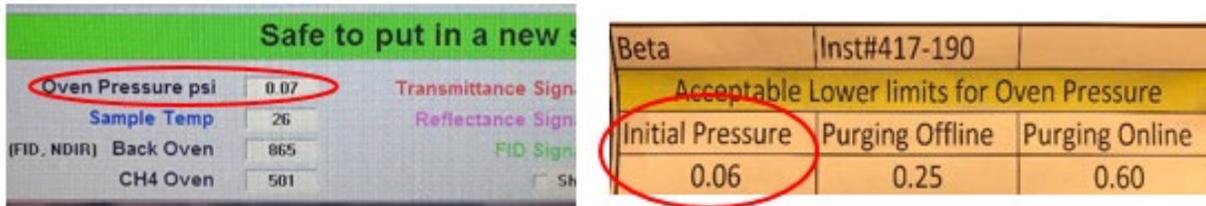


2. Identify the sample tray for the analyzer to be loaded. Take a Petri slide holder containing a quartz filter sample from the sample tray. Pick up the sample with metal forceps and place it in the sample punch area.
3. Clean the precision punch and metal forceps that handle the samples with a clean filter punch. Then use the precision punch to remove a section close to the edge of the deposited area (as opposed to in the middle of the filter). Cover the rest of the filter with the lid of the Petri slide holder immediately.

4. Use the sample removal tool to carefully lift half of the filter punch. Then use the metal forceps to transport the filter punch and place it on the sample holder. Make sure the sample (deposit) side is facing up and the punch lays flat.



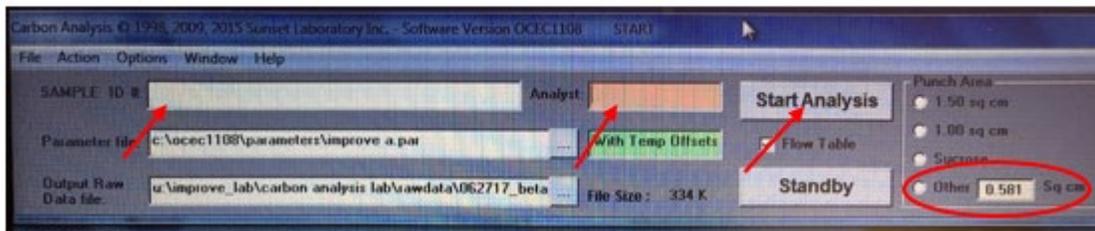
5. Use the silicone-coated forceps to *gently* slide the sample holder half way into the oven, then continue with the metal forceps until the sample holder is stopped by the tip of the oven thermocouple. Do not push the sample holder too hard or too fast, which could bend the thermocouple tip.
6. Seal the ball joint, making sure the O-ring seals tightly and place the clamp on the ball joint. Tighten the screw on the clamp finger.
7. Check the oven pressure on the software. It should read greater than or equal to the minimum value for the “Initial Pressure” specified for each analyzer. If not, tighten the clamp and/or re-adjust the O-ring position.



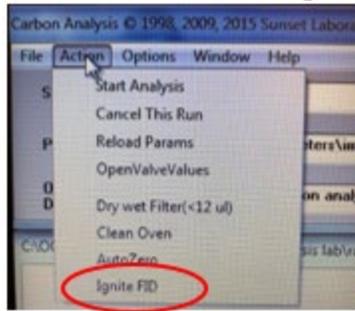
- At the computer, scan the barcode of a sample identification name (located on the petri slide holder) to fill in the Sample ID# field (make sure the Sample ID# field is highlighted) and type in the operator's initial in the Analyst field.



- Select **Other 0.568 sq cm** (or the most updated punch area) for punch area.



- Verify the FID is on by checking the signal reading (which should be >0) on the software or by placing a pair of metal forceps 1 cm above the FID chimney and look for water vapor condensation on the forceps surface. If the FID is off, click on "Action" menu and select "Ignite FID". Push the red ignition button on the methanator to light the FID, confirm with a soft "pop" sound if needed. Wait for the FID signal reading to increase above zero. If not, repeat the ignition.



11. Press the “**Start Analysis**” button. Move the mouse cursor away from “**Cancel run**” button.
12. Continue monitoring the oven pressure during the “Purging offline” and “Purging online” stages and make sure the threshold values are met or exceeded. If the oven pressure is lower than the threshold value at the end of “Purging online” stage, a warning message will appear and the software will pause until the threshold pressure is met or exceeded by re-adjusting the clamp or the O-ring position.

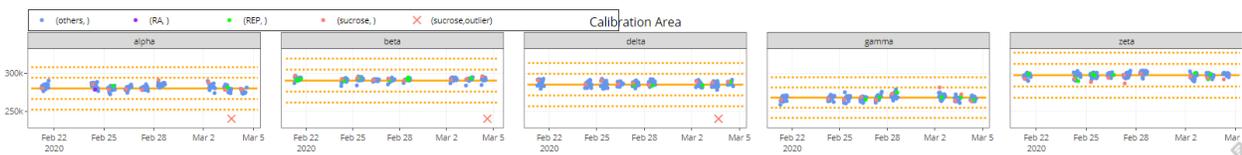
Beta	Inst#417-190	
Acceptable Lower limits for Oven Pressure		
Initial Pressure	Purging Offline	Purging Online
0.06	0.25	0.60

13. Enter the Log_date, Log_time, Sample ID and operator’s name in the logbook. Apply proper flag and input additional comment about atypical sample deposit and/or analysis issue through the CSN Data Management Site.
14. Return the filter sample to the Petri slide holder and move the Petri slide holder to the sample tray “DONE” section, orienting the holder in the opposite direction.



Analyzed sample pointing to the left

15. Mark the sample that is loaded on the sample list. Use one “x” for every punch that is taken. Then proceed to loading the next sample.
16. Continue monitoring the “FID signal” during all analyses. If the FID turns off during analysis, immediately click “Cancel run” and refer to step 10 to re-ignite the FID and make a note about it in the logbook. Once the FID is back on, repeat the analysis with a new punch from the same sample.
17. After finishing the analysis, check QC touchscreen to make sure the calibration areas are within $t \pm 10\%$ range of the instrument-specific daily mean value. If out of range, apply proper flag and comment through CSN Management Site, and reanalyze the sample. .



One exception is that, for extremely heavily loaded sample, readings from FID 2 channel are used for calibration, and the resulting calibration area is approximately $\frac{1}{4}$ of the normal value.

18. If the sample punch shows red/orange or gray/black color after analysis, save the punch, tape the punch to the “Colored Sample Logsheet” located on the wall, and fill in sample details. Apply proper flag through the CSN Management Site.

Running a replicate sample:

1. Approximately 5 % of the CSN samples are chosen to run a replicate analysis. These samples are highlighted on the sample tray list (every 20th network sample to be analyzed by each analyzer) and physically have “QC|REP” labels attached to their petri slides. One of the analyzers is randomly assigned to run the replicate punch.

2. For filter samples that are labeled “QC|REP|”, load the first punch to the designated analyzer as usual, and take an additional punch from the same filter and load it into the analyzer assigned.

NOTE: the assigned analyzer is selected randomly, and it may be the same analyzer that will run the first punch.

3. Type in “QC|REP|SampleID (scanning label)” in the Sample ID# box for the replicate sample punch and start analysis. Return the Petri slide holder to its original sample tray.
4. If the replicate analysis results for EC and OC do not meet the QC criteria summarized in Table 6 “Acceptance criterion for TC and EC replication analysis” in UCD CSN SOP

#402, reanalyze the 3rd punch from the same filter using an analyzer different than the original and replicate analyzers.

Running a weekly performance check sample:

1. Run a performance check (PC) sample every Wednesday morning (or more frequently as instructed). These samples are collected on 37 mm Quartz filters so they have sufficient deposit area for at least six punches.
2. Load one punch in each analyzer and run as normal sample. Type in “QC|PC|SampleID” in the Sample ID# box.
3. The measurement bias (%) of each analyzer is calculated by comparing its measurement with the average value obtained from the other five analyzers on the same PC sample. The average measurement bias for a given analyzer should be $\leq 10\%$ for TC and OC and $\leq 20\%$ for EC.

Stand-by at the end of day:

1. After finishing all analyses for the day, remove the filter punch from last run. Return the sample trays to the refrigerator.
2. Click on the “STANDBY” box on the instrument’ software. Wait until the gas flows drop down to preset levels (close to zero).
3. Check the gas cylinder pressures and record the values on the “Gas Pressure Table”. Close Air, Helium/Methane, and Hydrogen cylinders at their main valves.
4. Dispose the used foils and analyzed filter punches. Clean the working area with laboratory wipes.

10. QUALITY ASSURANCE AND QUALITY CONTROL

Not applicable.

11. REFERENCES

Not applicable.